Microwave Absorption and Molecular Structure in Liquids. LXXII. Dielectric Relaxations and Atomic Polarizations of Several Molecules Containing Librating Polar Groups[1]

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Abstract: Dielectric constant and loss measurements at centimeter and millimeter wavelengths have been made upon dilute solutions of six substances, the molecules of which contain dipolar groups capable of rotation or rotational oscillation. Bis(*p*-chloromethyl)benzene, as previously observed, shows a single, very short dielectric relaxation time characteristic of the rotation of the CH_2Cl. Bis(chloromethyl)durene shows an apparent small contribution from rotation of the hindered CH_2Cl group and a large contribution from rotation of the molecule as a whole. 1-Chloromethylnaphthalene, 1-naphthylacetonitrile, and 4-acetyl-*o*-terphenyl, which contain librating dipolar groups, show relaxation by rotation of the molecule as a whole, but have distribution parameters with values large enough to suggest a possible small contribution from rotation of the hindered dipolar groups. All of the molecules that contain dipolar, rotational oscillators show some elevation of the atomic polarization. Dinitrodurene shows only the very small dielectric loss which has been found to be characteristic of nonpolar molecules. The molecular dipole moment is, therefore, indistinguishable from zero, which shows the identity of the two nitrogen–oxygen bonds of the nitro group and the absence of any electrical dissymmetry of the molecule.

In the examination of dielectric relaxation by intramolecular rotation a number of cases have been observed in which steric repulsion has completely blocked or greatly hindered the complete rotation of a dipolar group about its bond to the rest of the molecule.[3–5] The shortest wavelength available for these measurements was 1.2 cm. With a 2.1-mm apparatus now available, it has seemed desirable to examine these molecules further to see if any relaxation by the rotational oscillation of the sterically blocked or hindered group could be detected. Two molecules in which resonance effects may play a part were also studied.

Experimental Section

Materials. 1-Chloromethylnaphthalene, obtained from K & K Laboratories, was recrystallized twice from cyclohexane and dried under vacuum.

Bis(*p*-chloromethyl)durene and 1-naphthylacetonitrile, obtained from K & K Laboratories and Eastman Kodak, respectively, were purified by the usual methods.[3,4]

Dinitrodurene, obtained from K & K, was recrystallized from benzene and dried in an Abderhalden pistol.

4-Acetyl-*o*-terphenyl, obtained from Eastman Kodak, was used after thorough drying under vacuum.

Apparatus and Methods. The apparatus has already been described in previous publications.[6–9] The static dielectric constant ϵ_0 was measured with a General Radio Co. low-frequency bridge (Type 1615A) at 10 kcps, and the refractive indices were measured with a Bausch and Lomb precision refractometer 33-45-02.

Results

Table I gives the dielectric loss ϵ' and dielectric constant e'' values of bis(chloromethyl)durene, dinitrodurene, and bis(*p*-chloromethyl)benzene in benzene solution. The mole fraction of solute or its range is shown in parentheses. The loss results are corrected for the small loss of the solvent. In the case of bis(chloromethyl)durene, the calculated values of ϵ' and ϵ'' for the best fit of the Cole–Cole plot obtained by an IBM computer give evidence of the precision of the measurements.

Table I. Dielectric Constants and Corrected Losses at 23° in Benzene Solution

λ_0, cm	ϵ'	ϵ'_{calcd}	ϵ''	$\epsilon''_{\text{calcd}}$
	Bis(*p*-chloromethyl)benzene (0.0171)[a]			
ϵ_∞	2.294			
0.21	2.298		0.0280	
1.25	2.350		0.0501	
3.22	2.378		0.0294	
10.01	2.389		0.0052	
50.00	2.390		0.0016	
3×10^6	2.390			
	Bis(chloromethyl)durene (0.0044)[a]			
0.21	2.284	2.282	0.002	0.002
1.25	2.285	2.286	0.005	0.005
3.22	2.288	2.290	0.007	0.009
10.00	2.301	2.301	0.012	0.012
25.00	2.308	2.308	0.007	0.007
50.00	2.311	2.309	0.003	0.004
3×10^6	2.3101			
	Dinitrodurene (0.0054)[a]			
0.21	2.284		0.0015	
1.25	2.284		0.0007	
3.22	2.283		0.0004	
10.01	2.284		≈0.0003	
3×10^6	2.2846			

[a] The mole fractions of solute are shown in parentheses.

Table II gives the slopes, a′ and a″, for the straight lines obtained by plotting ϵ' and ϵ'' for three solutions

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Table II. Dielectric Constant and Loss Slopes at 2.1 mm Wavelength and 20°, Relaxation Times, and Distribution Parameters

	a'	a''	a_∞	τ_0, 10^{-12} sec	α
1-Chloromethylnaphthalene (0–0.015)[a]	1.11	0.41	1.030	26.5	0.11
1-Naphthylacetonitrile (0–0.023)[a]	1.64	1.10	1.45	39	0.12
4-Acetyl-*o*-terphenyl (0–0.026)[a]	1.97	0.30	1.90	74	0.10
	τ_0, 10^{-12} sec	α	τ_1, 10^{-12} sec	τ_2, 10^{-12} sec	c_2
Bis(*p*-chloromethyl)benzene	3.0	0.01		3.0	
Bis(chloromethyl)durene (23°)	27.8	0.26	43.8	3.6	0.17

[a] The mole fraction ranges of solute are shown in parentheses.

Table III. Refractive Indices of Benzene Solutions and Polarization Values[a]

	nD	n_α	n_∞	P_E	MR$_D$	P_A
Bis(*p*-chloromethyl)benzene (0.0171)	1.5011	1.4969	1.4795	44.36	45.46	5.0
Bis(chloromethyl)durene (0.0044)	1.5001	1.4956	1.4772	62.70	63.98	8.6
1-Chloromethylnaphthalene (0.0152)	1.5035	1.4967	1.4784	52.06	54.82	9.2
1-Naphthylacetonitrile (0.0230)	1.5041	1.5001	1.4824	52.96	53.77	11.2
4-Acetyl-*o*-terphenyl (0.0259)	1.5154	1.5110	1.4928	82.11	84.56	8.0
Dinitrodurene (0.0054)	1.4999	1.4955	1.4771	56.03	56.77	12

[a] The mole fractions of solute are shown in parentheses.

of each substance against the mole fraction of solute. The infinite frequency slope value a_∞, the most probable relaxation time τ_0, and the distribution parameter α obtained from Cole–Cole plots are also given. For the first three substances in Table II, these quantities[10] are obtained by combining the 2.1-mm data with the measurements at longer wavelengths previously published.[3–5] Dinitrodurene is not included in Table II as its dielectric constant shows no frequency dependence and its very small losses are presumably associated with induced dipoles.[11] τ_1, the molecular relaxation time, τ_2, the intramolecular relaxation time, and c_2, the approximate fractional contribution of the intramolecular mechanism to the relaxation process, have been calculated as in previous work.[12]

Table III gives the refractive indices, nD and n_α, of the solutions for the sodium D line and the hydrogen α line, respectively, and the refractive index at infinite wavelength, n_∞, obtained from nD and n_α by means of the Cauchy dispersion equation.[10] The polarizations P of the solutes have been calculated from the usual equations for mixtures.[10] The induced polarization

$$P_I = P_E + P_A = [(\epsilon_\infty^2 - 1)/(\epsilon_\infty^2 + 2)](M/d)$$

where M is the molecular weight and d the density; the electronic polarization $P_E = [(n_\infty^2 - 1)/(n_\infty^2 + 2)]\cdot(M/d)$; and the atomic polarization $P_A = P_I - P_E$. The infinite-frequency dielectric constant ϵ_∞ is obtained as the high-frequency intercept of the Cole–Cole plot on the ϵ' axis.

Discussion of Results

The measurements on bis(*p*-chloromethyl)benzene and bis(chloromethyl)durene[3] gave particularly striking evidence of intramolecular group rotation and of the effect of steric hindrance upon this rotation. Because of the significance of this evidence for the further investigation of intramolecular rotation and steric effects, the measurements have been extended to 2.1 mm wavelength. The single relaxation time, 3.0×10^{-12} sec (Table II), found for bis(*p*-chloromethyl)benzene is in satisfactory agreement with the previously found value, 3.5×10^{-12}, and the negligible small value found for the distribution parameter α indicates that the most probable value, 3.0×10^{-12} corresponds to a single intramolecular relaxation by group rotation. This was indicated by the earlier measurements, although in those a considerable value of α suggested a possibility of a second relaxation mechanism. The single straight line for the plot[13] of ϵ' against $\epsilon''\omega$ in Figure 1 confirms the absence of any considerable contribution from a second relaxation process.

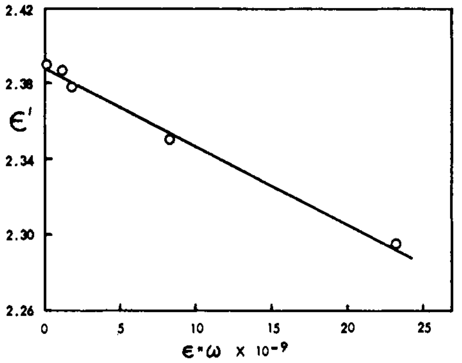

Figure 1. Plot of ϵ' against $\epsilon''\omega$ for solution of bis(*p*-chloromethyl)benzene (mole fraction 0.0171) at 23°.

As shown by the two intersecting lines in Figure 2, bis(chloromethyl)durene, in which the CH_3 groups on each side of the CH_2Cl groups strongly hinder the rotation of the latter, has two relaxation processes (Figure 3). For the slower process, the time τ_1 (Table II) is indistinguishable from that previously reported and attributed to over-all molecular rotation. For the shorter process

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(10) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(11) S. K. Garg, J. E. Bertie, H. Kilp, and C. P. Smyth, *J. Chem. Phys.*, in press.

(12) K. Bergmann, D. M. Roberti, and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).

(13) R. H. Cole, *J. Chem. Phys.*, **23**, 493 (1955).

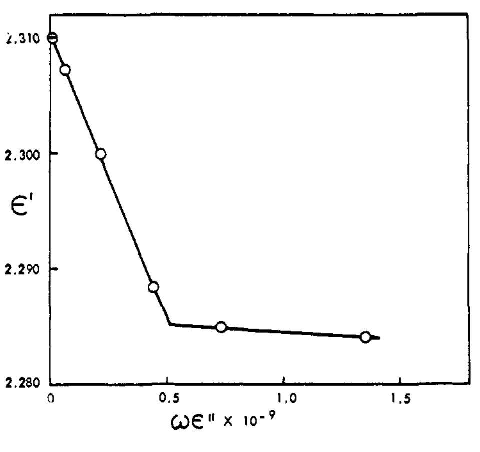

Figure 2. Plot of ϵ' against $\epsilon''\omega$ for solution of bis(chloromethyl)durene (mole fraction 0.0044) in benzene at 23°.

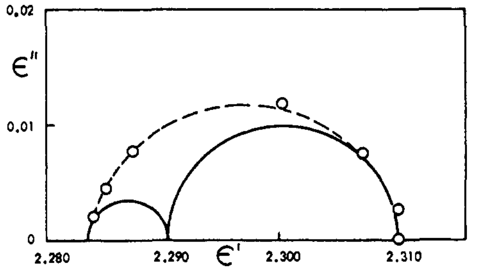

Figure 3. Cole–Cole plot for solution of bis(chloromethyl)-durene (mole fraction 0.0044) in benzene at 23°.

which escaped detection in the absence of the 2.1 mm measurement and contributes only about 17% of the total relaxation, the time τ_2 is indistinguishable from that found for bis(p-chloromethyl)benzene, in which it is almost certainly associated with the rotation of the CH$_2$Cl groups around their bonds to the ring. In the Stuart–Briegleb model of the molecule, the methyl groups force the chlorine atoms into *cis* or *trans* positions with respect to the plane of the ring and seem normally to block complete rotation, while permitting a considerable rotational oscillation. As pointed out previously, the *cis* form of the molecule has a dipole moment which will cause it to orient in an applied electric field, showing the long relaxation time τ_1. The nmr spectrum of bis(chloromethyl)durene has been interpreted as showing exchange about 1000 times a second between the *cis* and *trans* forms,[14] but this intramolecular change is slower by a factor of 3 × 10^8 than the shorter relaxation process observed here. It would appear that the extent of the dipole orientation produced by rotation of the CH$_2$Cl group is considerably reduced (c_2 = 0.17) by the steric blocking exerted by the CH$_3$ groups, but the time required for it, τ_2, is practically unchanged from that in bis(p-chloromethyl)benzene, in which there is no blocking. The atomic polarization of bis(chloromethyl)durene is 70% higher than that of bis(p-chloromethyl)benzene, a difference larger than that to be expected from the contributions of the four methyl groups in the former.

The values of the single relaxation time and the distribution parameter α for 1-chloromethylnaphthalene

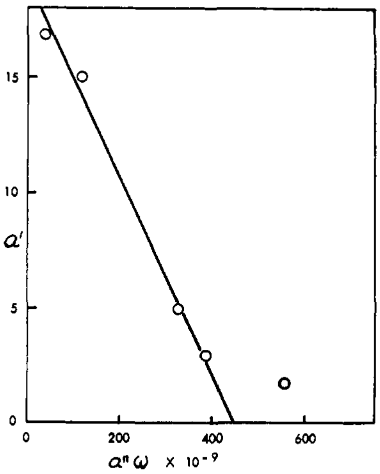

Figure 4. Plot of a' against $a''\omega$ for solutions of naphthylacetonitrile in benzene at 20°.

in Table II are in close agreement with those previously found in this laboratory, which indicated only an overall molecular relaxation process.[4] However, the large atomic polarization 9.2 in Table III shows the presence of an exceptionally large absorption in the infrared region. In the case of 1-naphthylacetonitrile, the value found for the relaxation time is higher than that found previously[4] and the 2.1-mm point in Figure 4 lies considerably above the straight line drawn through the points for lower frequencies, indicating a second relaxation process, perhaps involving the rotational oscillation of the CH$_2$CN group, which, to an even greater extent than the CH$_3$Cl group, is sterically repelled by the hydrogen in the 8 position. This oscillation may also be responsible for the large atomic polarization (Table III), which is higher than that of 1-chloromethylnaphthalene, presumably because the dipole moment of the CH$_2$CN group is larger than that of the CH$_2$Cl group.

In the earlier work on 4-acetyl-o-terphenyl[5] the results were analyzed to obtain a molecular relaxation time τ_1 = 100 × 10^{-12} sec with indication of a small contribution (12%) from an intramolecular process having a relaxation time τ_2 = 7.5 × 10^{-12} sec. The larger value of τ_0, 74.2 × 10^{-12} sec, and small value of α, 0.10, in Table II indicate that the principal relaxation process is that of molecular rotation. As the Stuart–Briegleb model of the molecule shows that the acetyl group is free from any steric hindrance to its rotation, the absence of a large contribution to relaxation from rotation of the CH$_3$CO group may be attributed as before[5] to a potential barrier arising from resonance energy. The large size of the atomic polarization, P_{A} = 8.0 cc, is attributable to the librational motion of the polar group, as in the cases of the other molecules in which the hindrance to free rotation is steric repulsion. Although the actual atomic polarization of 1-acetonaphthone was not determined in the earlier work,[5] the large difference between the slopes a_∞ and a_{D} was interpreted as evidence of a large atomic polarization associated with libration of the sterically blocked CH$_3$CO group. Although the enhancement of atomic polarization by the presence of a librating polar group is not very large, it appears that each of these five molecules with librating polar groups has an atomic polarization some 2–4 cc above normal.

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(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223.

Dinitrodurene was examined with a double objective. As the molecule appears to be symmetrical, one might expect zero dipole moment as in the case of *p*-dinitrobenzene.[15,16] However, the dipole moment of nitrodurene was found[17] to be 3.39 D, in close agreement with the moments of the nitroparaffins and much smaller than that of nitrobenzene, 3.98 in solution and 4.21 in the vapor.[10] Also the moment of *p*-aminonitrodurene[17] is 4.98 as compared to 6.2 for *p*-nitroaniline. It was suggested[17–19] that steric repulsion between the methyl groups of nitrodurene and the oxygens of the nitro group forced the nitro group to rotate its oxygens out of the plane of the ring, thus eliminating or reducing the double-bond character of the C–N bond and the resonance contributions of the polar structures thought to be responsible for the elevation of the dipole moment above those of the nitroparaffins. If there were any difference between the two nitrogen–oxygen bonds of the nitro group, this forcing of the plane of the nitro group out of that of the ring would result in the existence of *cis* and *trans* isomers of dinitrodurene somewhat analogous to those thought to exist in bis(chloromethyl)-durene. The *cis* isomer would have a dipole moment which would give rise to readily measurable frequency dependence of the dielectric constant and loss of the dilute solution in Table I. The dielectric constant values of the dinitrodurene solution in Table I show no dependence on frequency and the very small loss values, corrected for the loss of the nonpolar solvent benzene, show the increase with frequency through the 2-mm region which has been found to be characteristic of nonpolar liquids.[11] There is, therefore, no evidence of a polar *cis* form and, consequently, no evidence of any difference between the two nitrogen–oxygen bonds of the nitro group in dinitrodurene. This same lack of evidence for the existence of a polar form also points to the absence of any unsymmetrical structure in the liquid in which the nitro groups are bent out of the plane of the ring either by bending of the C–N bonds or by deformation of the ring.

The rather approximate value of the atomic polarization of *p*-dinitrodurene, $P_A = 12$ cc, is higher by 3 cc than that of *p*-dinitrobenzene.[20] Although this difference is only a little larger than that which might arise from experimental error, it may be noted that approximate atomic polarization values calculated from early polarization values of Tiganik[21] show an increase of 2.9 cc from the value 10.7 for 1,3,5-trinitrobenzene to 13.6 for 1,3,5-trimethyl-2,4,6-trinitrobenzene. This contrasts oddly with the absence of significant difference between 0.7 cc for 1,4-dimethylbenzene, 0.5 for 1,3,5-trimethylbenzene, and 0.6 for hexamethylbenzene also calculated from Tiganik's measurements. In straight-chain alkanes the atomic polarization[20] is only 0.07 cc for CH_2. It would appear, therefore, that the rise in atomic polarization from 5.0 for bis-*p*-chloromethylbenzene to 8.6 for bis(chloromethyl)durene is significant. Similarly, the rise from 3.0 for 1-chloronaphthalene[22] to 9.2 for 1-chloromethylnaphthalene (Table III) is even more significant. In the latter molecule, a wider rotational oscillation of the polar group can occur, apparently permitting a greater contribution to atomic polarization than that made by the two more restricted CH_2Cl groups in bis(chloromethyl)durene. The structure of 1-naphthylacetonitrile is similar to that of 1-chloromethylnaphthalene, but the larger dipole moment of the CH_2CN group gives a higher atomic polarization than that given by the CH_2Cl group.

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(15) Reference 10, p 324.

(16) E. N. Di Carlo and C. P. Smyth, *J. Am. Chem. Soc.*, **84**, 1128 (1962).

(17) R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, 10 (1957).

(18) C. E. Ingham and G. C. Hampson, *ibid.*, 981 (1939).

(19) Reference 10, p 328.

(20) Reference 10, p 420.

(21) L. Tiganik, *Z. Physik. Chem.*, **B13**, 425 (1931).

(22) S. K. Garg and C. P. Smyth, *J. Chem. Phys.*, **42**, 1397 (1965).